Measurement of Conduction-Electron Spin Relaxation Due to Rare Gases Physisorbed on a Lithium Surface

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The conduction-electron spin-scattering cross sections of krypton and xenon atoms adsorbed on a lithium surface were determined by measurement of the conduction-electron spin-resonance linewidth of lithium films as a function of rare-gas coverage. The results indicate that there is a large pileup of conduction-electron density deep within the rare-gas adsorbate core, in agreement with current theoretical calculations of the electronic structure of rare-gas-on-metal systems.

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The spin orientation of a conduction electron at the Fermi surface may change when the electron collides with an adsorbate on the surface of a metal. The ability to perform quantitative electron spin surface relaxation (QUESSR) measurements of this spin-relaxation process provides a new tool with which to probe the adsorbate–metal-surface complex, and is the subject of this Letter.

The utility of knowing an adsorbate's spin-scattering cross section derives from the nature of the scattering mechanism. Conduction-electron spin scattering by nonmagnetic adsorbates is due to spin-orbit interaction which will only be appreciable in a very small volume surrounding the adsorbate nucleus.[1] Thus, an adsorbate's spin-scattering cross section will reflect the extent to which the Fermi-level conduction-electron wave functions overlap the adsorbate core. Magnetic adsorbates will have an additional spin-scattering component due to the exchange interaction, which may be expected to provide information concerning the formation and ordering of surface local moments.

In this Letter we present measurements which demonstrate that conduction-electron spin resonance (CESR) may be used to measure spin scattering by adsorbates over a broad range of coverage, and, in the limit of dilute coverage, may be used to determine the adsorbate's spin-scattering cross section. We have measured the spin-scattering cross sections of krypton and xenon physisorbed on polycrystalline lithium films prepared in UHV, and have set upper limits for the cross sections of argon and neon. Our results indicate that there is a pileup of conduction electron density within the rare-gas adsorbate core.

Previous efforts to measure what is generally referred to as surface spin relaxation have been aimed at determining either that which is intrinsic to a bare metal surface,[2] or that which occurs at an interface between two metals.[3] In contrast to the present work, none of these previous investigations were performed with the atomically clean surfaces and controlled fractional monolayer coverage of adsorbates necessary to derive quantitatively meaningful results. Recent transport measurements by Bergmann[4] demonstrating spin scattering by Au atoms on an ultrathin Mg film exhibiting weak localization have been performed under UHV conditions.

The CESR linewidth, $\Delta H = 1/\gamma T_2$, of a metal sample in the form of a uniform film of thickness L, will have a component, ΔH_s, due to surface spin relaxation on one side of the film given by[5,6]

$$\Delta H = \Delta H_B + \Delta H_s = \Delta H_B + \frac{\epsilon(1+B_0)v_F}{2(2-\epsilon)\gamma L}, \tag{1}$$

where ϵ is the probability that an electron's tranverse spin orientation is lost in a collision with the surface,[7] v_F is the Fermi velocity, B_0 is the first Landau spin parameter, γ is the electron gyromagnetic ratio, T_2 is the transverse spin relaxation time, and ΔH_B is the linewidth due to all other spin relaxation processes. ϵ will depend on the adsorbate coverage, θ (atoms/cm^2), and for dilute enough coverage will be linear in θ according to $\epsilon = \sigma\theta$, where σ is the surface spin-scattering cross section of an adsorbate which is effective in relaxing transverse spin magnetization.[8]

The experiments were conducted with the apparatus shown in Fig. 1. A continuous-flow, nonmagnetic, liquid-helium cryostat was constructed which would allow the *in situ* measurement of the CESR signal of samples prepared and maintained in UHV, and at any temperature in the range 4–400 K.[6] The ion/sublimation-pumped vacuum system has a base pressure near the cryostat of 3×10^{-11} Torr *prior* to the attainment of cryogenic temperatures. The Li sample is typically evaporated onto a 4-K sapphire substrate which forms part of one wall of a 9-GHz TE$_{101}$ microwave cavity, and which has had a prior coverage of Li and LiF to reduce spin relaxation at the substrate. The CESR signal is recorded immediately after deposition of the Li sample in order to establish an initial linewidth. The sample (at 4 K) is then dosed in increments (starting with a small fraction of a monolayer) of the gas to be studied. The CESR signal is measured after each dose. A 6-MHz quartz-crystal microbalance, maintained at the same temperature as the sample, is used to determine both the sample thickness and the adsorbate coverage.

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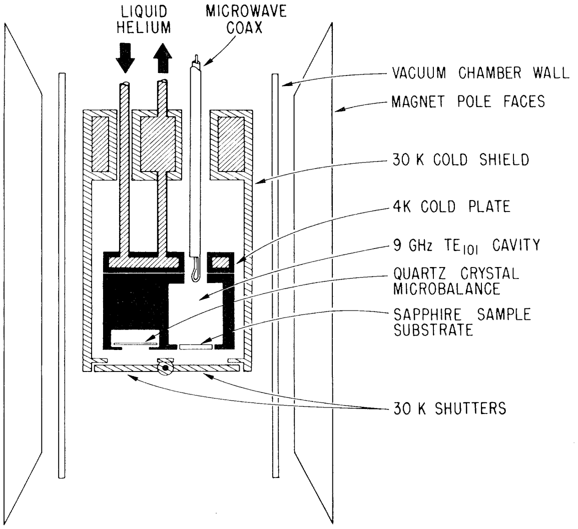

FIG. 1. A schematic view of the apparatus for measurement of the CESR signal of samples prepared in UHV. The shutters (shown in the closed position) are open to allow the deposition of the Li film and adsorbate. Provisions for measuring and regulating temperature, for multiple sample substrates, for redirecting the flow of helium so as to bypass the "cold plate," and for actuating the shutters have not been shown for reasons of clarity.

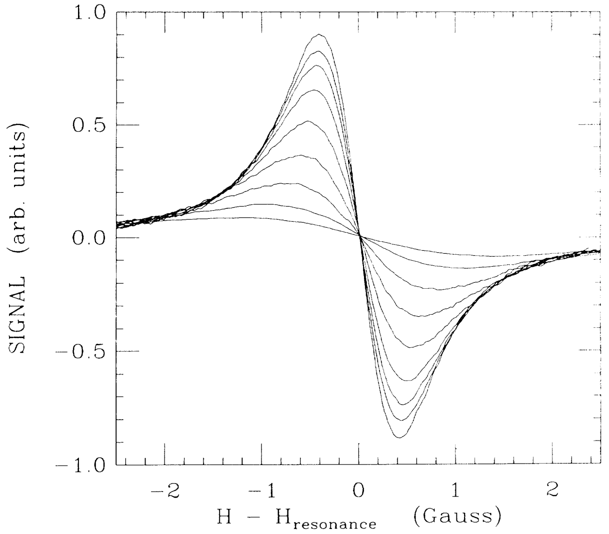

FIG. 2. An example of the broadening of the 4-K CESR signal of a 0.4-μm-thick Li sample due to spin scattering by adsorbed Xe. In order of increasing linewidth (decreasing amplitude) the signals are recorded with the following Xe coverages: 0, 5×10^{12}, 1×10^{13}, 2×10^{13}, 4.2×10^{13}, 8.3×10^{13}, 1.64×10^{14}, 3.22×10^{14}, and 6.31×10^{14} atoms/cm^2. The decrease in signal amplitude is in precise accord with the increase in linewidth. After desorption of the Xe at 53 K, the 4-K signal returned to the initial zero-coverage line shape.

In Fig. 2 we demonstrate the broadening of the 4-K CESR signal of a 0.4-μm-thick Li sample due to adsorbed Xe. After attainment of a coverage of several layers, the sample was heated until the rare gas desorbed (as monitored with a mass spectrometer). The ability to reversibly modulate the rare-gas coverage provided an unambiguous signature to the adsorbate spin-scattering component of the resonance linewidth. The adsorption-desorption process was repeated as a measure of reproducibility, and as a test for time-dependent surface contamination.

Figure 3 displays values of ϵ [as deduced from the data via Eq. (1)] as a function of the gas coverage, θ, for Xe and Kr. From the low-coverage ratio of ϵ to θ we determine the spin-scattering cross sections of Kr and Xe to be $(2\pm1)\times10^{-20}$ and $(3.5\pm0.7)\times10^{-19}$ cm^2, respectively. ϵ is seen to deviate from being linear with θ at coverages as small as 5×10^{13} cm^{-2}, to smoothly increase through monolayer coverage ($\sim8\times10^{14}$ cm^{-2}), and to saturate to coverages corresponding to roughly ten layers. A variety of mechanisms could be responsible for the increase in ϵ due to the second and higher adsorbate layers, for example, a compaction of the first layer toward the metal due to higher layers, an electronic modification in the first layer due to the presence of higher layers, spin scattering at the second and higher layers, etc. The present data not allow the ability to distinguish which mechanism(s) is (are) responsible.

Ne and Ar were also investigated, but yielded no measurable line broadening.[9] After desorption of these gases from the samples on which they were stud-

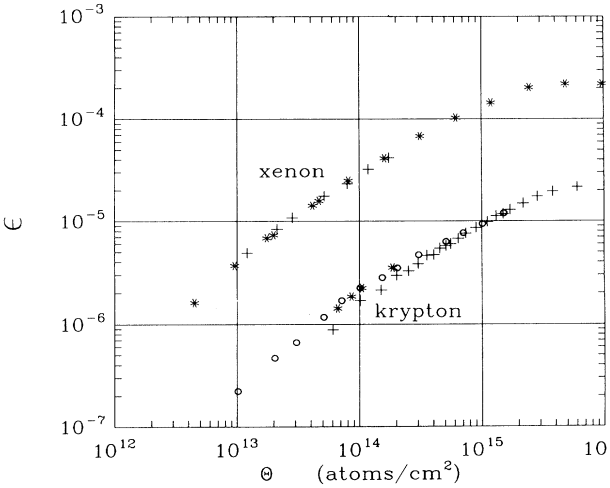

FIG. 3. The probability of spin scattering per collision with the surface, ϵ, vs the gas coverage, θ, for Kr on Li, and Xe on Li. The circles, asterisks, and crosses indicate data taken on different Li samples. The low-coverage ratio of ϵ to θ yields the spin-scattering cross section.

ied, the line broadening due to a fractional monolayer dose of Xe was used to quantitatively certify that the null result was not due to sample conditions or some unknown error. The upper limit for the spin-scattering cross sections of Ne and Ar on Li is 1×10^{-21} cm^2, as determined by the estimated minimum detectable line broadening under the conditions in which the experiments were performed.

The measured spin-scattering cross sections rank according to atomic number, consistent with the very rapid increase in the spin-orbit interaction. It is found that the rare-gas surface spin-scattering cross sections are *only* between 1 and 2 orders of magnitude smaller than the bulk spin-scattering cross sections of metallic elements of comparable atomic number.[10] At first glance this is a surprising result. Rare-gas atoms are bound at a distance from the metal surface where the bare-metal conduction-electron density is typically reduced from its mean bulk value by between 2 and 3 orders of magnitude,[11] leading one to estimate a reduction in spin-scattering cross sections by 4 to 6 orders of magnitude. It becomes increasingly more difficult to reconcile the size of the cross sections if one considers the rare-gas atom to act only as a repulsive pseudopotential which locally displaces conduction-electron density.[11,12] The magnitude of the experimentally determined rare-gas spin-scattering cross sections can only be accounted for by an enhancement of the $l > 0$ components of the Fermi-level conduction-electron wave functions in the rare-gas core relative to the bare-metal wave functions. From this we deduce that there is a large pileup of conduction-electron density in the rare-gas adsorbate core.

This pileup in density was, to our knowledge, first explicitly discussed by Zaremba and Kohn,[13] who considered the binding of He to a metal which was modeled as jellium. Using the density functional method, Lang[11] and Lang and Nørskov[12] have calculated the electron structure of rare-gas atoms bound to metal surfaces. We have examined the conduction-electron density at adsorbed rare-gas atoms utilizing the computer program of Lang and Williams.[14] Figure 4 is a plot of the calculated *conduction-electron* density normal to the surface of a metal modeled as $r_s = 3$ jellium and through the center of a Kr atom which was chosen to be at a distance of 4.75 bohrs[15] from the positive background edge.[16] The $r_s = 3$ bare-metal density (dashed curve) is presented to emphasize the form and extent of the conduction-electron density redistribution which is caused by the rare gas. We take the measured spin-scattering cross sections to qualitatively confirm the buildup of conduction-electron density in the rare-gas adsorbate core displayed in Fig. 4. Comparison of our measurements with calculations by Lu, Sham, and Shore[17] of the spin-scattering cross sections should allow an accurate determination of the equilibrium distance of the adsorbate nucleus from the substrate.

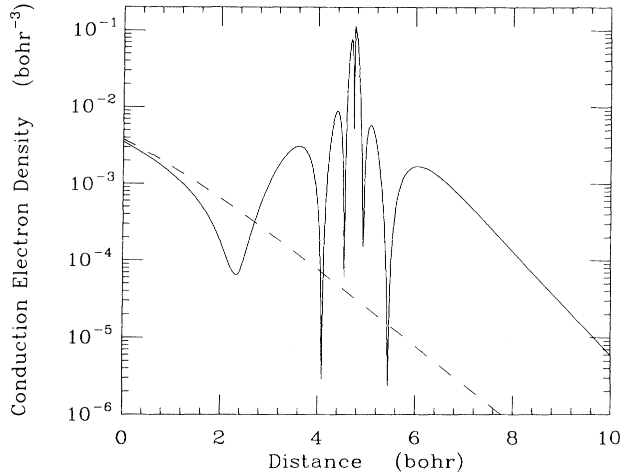

FIG. 4. The calculated conduction-electron density normal to the surface and through the nucleus of a krypton atom adsorbed at a distance, *d*, of 4.75 bohrs, measured from the positive background edge of a metal modeled as $r_s = 3$ jellium (solid curve). The bare-metal conduction-electron density (dashed curve) is shown for reference.

We have demonstrated how CESR may be used to measure spin scattering of conduction electrons by adsorbates, and how spin-scattering cross sections may be used as a measure of the electronic structure at adsorbate atoms. The QUESSR technique is, in principle, applicable to all the metals in which CESR may be observed, and should be readily extendable to highly doped semiconductors. Initial studies with metallic adsorbates have demonstrated an extreme sensitivity (e.g., we can detect less than 10^{-6} monolayers of W), which should allow studies of configurational changes of adsorbed complexes containing high-atomic-number elements. Bulk spin-scattering cross sections may also be measured by "burial" of the adsorbed impurity atoms with additional host material. Preliminary experiments with magnetic adsorbates have already validated the applicability of the technique for studying surface local moments.

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[8] A conduction electron's wave function will have strong anisotropic components at an adsorbate atom which are expected to cause the measured spin-scattering cross section to have a dependence on the angle between the applied magnetic field for resonance and the surface normal. All of our measurements were conducted with the field parallel to the sample surface. For an explanation see Eigler (Ref. 6) and Y. Yafet (to be published).

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